(51) International Patent Classification 5 :		(11) International Publication Number:	**WO 93/06038**
C01B 7/09	**A1**	(43) International Publication Date:	1 April 1993 (01.04.93)

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(54) Title: PROCESS FOR PRODUCING BROMINE FROM SEAWATER
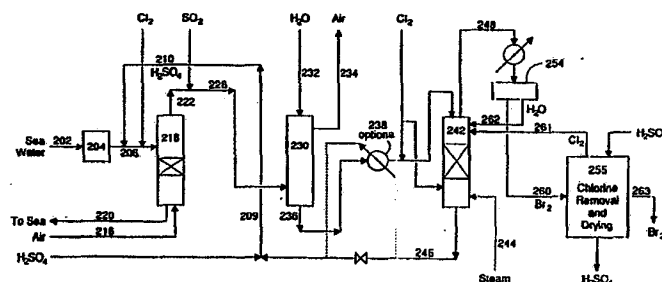
(57) Abstract

This invention is a combination process for producing elemental bromine using a seawater feed. The process involves a series of steps in which seawater is acidified, chlorinated, and air stripped to remove the bromine. The stripping effluent is reacted with an SO_2 stream to convert the bromine to hydrogen bromine and H_2SO_4 in the air stream. The process continues by absorbing hydrogen bromide and H_2SO_4 from the resulting acidic fog to produce an aqueous H_2SO_4 stream containing HB_r. The HB_r is stripped from the liquid stream and passed to an oxidation reactor where it is catalytically oxidized with an oxygen-containing gas to produce a stream of Br_2 and H_2O. The hot reactor effluent is quenched and the product Br_2 is separated from the H_2O and inert gases such as air. In the figure 2 seawater enters pipeline (202) and is mixed with an H_2SO_4 stream (200). The resulting stream (214) is sent to a stripping column (218) where air stream (216) strips the bromine from the liquid. The vapor B22 stream (222) is mixed with SO_2 (224) which is contacted with a water stream. The resulting aqueous H_2SO_4/HBr stream (236) is heated and mixed with a chlorine stream (240). A portion of the chlorine is introduced through line (241) to the bottom of stripping column (242) and separates with stream (244) into stream (246) containing H_2O_4 and HCl separates with stream (244) into stream (246) containing H_2SO_4 and HCl and stream (248) containing Br_2. The Br_2 product (260) is discharged from decanter (254) into the purification unit (255).

5   PROCESS FOR PRODUCING BROMINE FROM SEAWATER

Field of the Invention
               This invention is a combination process for
       producing elemental bromine using a seawater feed. The
10   process involves a series of steps in which seawater is
       acidified, chlorinated, and air stripped to remove the
       bromine. The stripping effluent is reacted with an SO_2
       stream to convert the bromine to hydrogen bromide and
       H_2SO_4 in the air stream. The process continues by
15   absorbing hydrogen bromide and H_2SO_4 from the resulting
       acidic fog to produce an aqueous H_2SO_4 stream containing
       HBr. The HBr is stripped from the liquid stream and
       passed to a oxidation reactor where it is catalytically
       oxidized with an oxygen-containing gas to produce a
20   stream of Br_2 and H_2O. The hot reactor effluent is
       quenched and the product Br_2 is separated from the H_2O and
       any inert gases such as air,

Background of the Invention
25   This invention is a process for producing
       elemental bromine from hydrogen bromide recovered from
       seawater involving a catalytic oxidation step. The
       catalytic oxidation step permits the inventive process to
       eliminate nearly 50% of the chlorine requirements of the
30   known processes.
               Bromine is a chemical feedstock often used for
       the production of bromoalkanes or olefins from alkanes.
       Bromine is present in nature only in dilute sources such
       as in seawater or in brines of the Dead Sea or the United
35   States. The classic process for producing bromine from

seawater involves a multistage process of acidifying and
chlorinating the brine to release elemental bromine into
a solution; aerating the resulting dilute solution;
reacting the bromine with SO_2 to produce hydrogen bromide

5   and sulfuric acid; absorbing the hydrogen bromide and
sulfuric acid from the aeration effluent into water;
heating, chlorinating, and steaming the resulting
absorbate; stripping the bromine overhead; and decanting
the resulting overhead product to recover the bromine.

10   This invention includes a catalytic process sequence
which may be inserted into the classic process as a
substitute for the steps of heating, chlorinating, and
steaming the aeration effluent. The process steps may
include:

15   (a) stripping the aeration effluent to produce
an HBr/H_2O stream,
             (b) catalytically oxidizing the HBr/H_2O stream
to produce a wet Br_2 stream, and
             (c) separating the Br_2 from the water.

20

We know of no process in which elemental bromine is
produced from seawater and which uses a catalyst to
produce the desired Br_2.

             There are a number of processes described in

25   the open literature which produce bromine according to
the equation:

$$4 \ HBr + O_2 \ ---> 2 \ Br_2 + 2 \ H_2O.$$
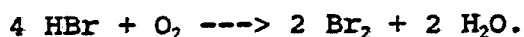
             One such process (British Patent 930,341)
involves the conversion of hydrobromic acid solutions

30   using dissolved metal ion catalysts. The soluble metal
may be gold, cerium, chromium, nickel, platinum, thorium,
titanium, or vanadium; but preferably is iron or copper.
A gas containing oxygen is passed through the acidic
solution containing HBr and the dissolved metal, all at a

35   temperature below the boiling point of the liquid. The

gaseous effluent is then separated via condensation and
distillation into product bromine, water, and HBr for
recycle to the oxidation step.

Similarly, U.S.Pat.No. 3,179,498, to Harding et
5   al, disclose a process in which a nitrite catalyst is
employed in the acidic, aqueous solution of HBr to effect
the oxidation of the HBr to Br_2. The temperature of the
liquid is maintained between 0° and 100°C. Although any
inorganic or organic nitrite is said to be suitable,
10   preferred catalysts are alkali or alkaline earth metal
nitrites.

There are a number of processes which use
heterogeneous catalysts to effect that conversion.

U.S. Pat. No. 2,536,457, to Mugdan, teaches
15   such a process. The conversion is carried out at a
temperature between 800° and 1200°C (preferably between
800° and 1000°C) with an excess of oxygen. The catalyst
is preferably cerium oxide and may be supported on pumice
granules or other refractory materials. If excessive
20   water is included in the reactor, a combustible gas such
as hydrogen is included to maintain the reaction
temperature. Clearly the reaction temperature for this
process is quite high.

U.S. Pat. No. 3,273,964, to De Rosset, shows a
25   process in which the effluent from a dehydrobromination
reaction is contacted with a catalyst-adsorbent
composite. The effluent contains olefinic hydrocarbons
and is produced by a series of steps in which an alkane
is brominated to form a bromoalkane; the bromoalkane is
30   then dehydrobrominated to form the effluent of olefinic
hydrocarbons and HBr. The catalyst-adsorbent composite
adsorbs the HBr in a first step and, during regeneration,
catalyzes the oxidation of HBr to form the desired Br_2.
The composite contains an adsorbent of a basic metal
35   oxide such as magnesium, calcium, or zinc oxide, and a

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catalyst of a Group IV-B metal oxide such as titania,
magnesia, or zirconia. The preferred composite contains
magnesia and zirconia in a ratio from about 0.5:1 to
about 5:1.

5   U.S. Pat. No. 3,260,568, to Bloch et al,
teaches a process in which a stream containing
substantially dry HBr contacts a solid adsorbent
containing a metal "subchloride" and which is the
reaction product of a refractory metal oxide and a metal

10   chloride. The contact takes place at conditions where
the HBr replaces at least a portion of the chloride in
the adsorbent. When the adsorbent has reached about six
percent by weight, the adsorbent is regenerated by
contacting it with a dry hydrogen chloride gas. The

15   patent does not appear to suggest the conversion of the
adsorbed HBr to Br_2 even though the adsorbent is
suggested to be selected from metal chlorides such as
aluminum, antimony, beryllium, iron, gallium, tin,
titanium, and zinc chlorides.

20   U.S. Pat. No. 3,310,380, to Lester, discloses a
process for the adsorption of combined bromine (e.g., HBr
and alkyl bromides) on a catalytic-adsorbent composite,
recovering unsaturated hydrocarbons, and when the
adsorbent is filled, contacting the composite with an

25   oxygen-containing gas at a temperature between 50° and
450°C to produce a Br_2 stream also containing water and
unreacted HBr. This stream (also in admixture with an
oxygen-containing gas) is then contacted with a second
stage reactor also containing the composite but at a

30   temperature between 200° and 600°C. The composite in the
first stage comprises, preferably, 0.5 to 10% by weight
of copper or cerium oxide composited on magnesium oxide:
the second stage composite comprises, preferably, 2.0 to
about 50% by weight of copper or cerium oxide composited

35   on an alumina or zirconia support.

Similarly, U.S. Pat. No. 3,346,340, to Louvar
et al, suggests a process for the oxidation of HBr to Br_2
using a catalyst-inert support composite. The composite
comprises a copper or cerium oxide on an inert support
5   having a surface area between 5 and 100 square meters per
gram and containing less than about 50 micromoles of
hydroxyl per gram. The supports may be alpha- or theta-
alumina or zirconia. The preferred temperature is
between 300° and 600°C.

10   U.S. Pat. No. 3,353,916, to Lester, discloses a
two stage process for oxidizing HBr to form Br_2 by the
steps of mixing the HBr-containing gas with an oxygen-
containing gas and passing the mixture at a temperature
of at least 225°C over a catalyst selected from the
15   oxides and salts of cerium, manganese, chromium, iron,
nickel, and cobalt and converting a major portion of the
HBr to Br_2. The partially converted gas, still
containing excess oxygen, is then passed through a second
stage catalyst comprising a copper oxide or salt at a
20   temperature of at least about 225°C but not exceeding a
"catalyst peak temperature" of 350°C to convert the
remaining HBr. The preferred support appears to be
zirconia.

This two-stage arrangement is carried out to
25   prevent loss of copper catalyst. Because the preferred
copper oxide is converted to copper bromide during the
course of the reaction, at reaction conditions, and
copper bromide volatilizes at "temperatures in excess of
about 350°C", the "copper bromide migrates through the
30   catalyst mass in the direction of flow with eventual loss
of copper bromide and premature deactivation." Use of a
first catalyst stage which is tolerant of high
temperatures, even though the first stage catalyst is
apparently not as active a catalyst as is copper, allows
35   a cooler second catalyst stage containing copper to

complete "quantitative conversion of bromine from
hydrogen bromide."

U.S. Pat. No. 3,379,506, to Massonne et al,
discloses a process for the selective oxidation of
5   hydrogen bromide to bromine in the presence of
fluorocarbons by passing the mixture of gases over a
Deacon catalyst at a temperature of 250 to 475°C,
preferably between 300 and 400°C. The Deacon catalyst is
said to be a "mostly porous carrier such as pumice,
10   alumina, silica gel, clay, or bentonite, impregnated with
a solution of bromides or chlorides of metals such as
copper, iron, titanium, vanadium, chromium, manganese,
cobalt, molybdenum, tungsten, or mixtures thereof." The
preferred catalyst is said to be a chloride of copper.
15   The patent notes that

"[a] very efficient and stable catalyst is an
oxidation catalyst which is prepared by
impregnating active alumina with chlorides of
copper, rare earths and\or alkali metals,
20   drying at about 120°C and subsequent activation
at a temperature of 300° to 450°C."
One example shows the production and use of a catalyst of
alumina, potassium, copper, and an amount of "rare earths
of the cerite group as chlorides".
25   Another patent which notes the problem with the
volatilization of copper bromide in the oxidation of
hydrogen bromide to bromine is U.S. Pat. No. 3,437,445,
to Hay et al. The solution is to eliminate the copper in
favor of a noble metal, such as platinum and palladium.
30   The reaction is carried out at a temperature of about
175° and about 700°C with a contact time of at least
about 0.1 sec, "but for best operation a contact time of
about five and 25 seconds is preferred." The yield of
bromine is only between 28 and 78 molar percentage.
35

U.S. Pat. No. 4,131,626, to Sharma et al,
suggests a process in which bromide salts are heated in
the presence of an oxygen-containing gas, silicon
dioxide, and an oxidation catalyst at a temperature of
5   about 500° to 1000°C. The bromine is produced in
conjunction with sodium silicate.

None of these documents suggest a process in
which Br_2 is produced from seawater using a catalytic HBr
oxidation step.
10

Summary of the Invention

This invention is a process for producing Br_2
from seawater in which an intermediate catalytic step
comprises oxidizing hydrogen bromide with O_2 to form that
15   elemental bromine.

In this process, seawater is screened of solid
material such as seaweed and fish and acidified with H_2SO_4
to produce an acidified stream having a pH between 3.0
and 3.5. This improves bromine recovery by suppressing
20   the hydrolysis of bromine as it is formed:

$$Br_2 + H_2O \ \text{-->} \ HBr + HBrO.$$
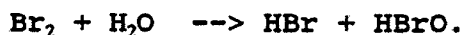
The bromide ion in the seawater is then oxidized using
chlorine:

$$2 \ Br^- + Cl_2 \ \text{-->} \ Br_2 + 2 \ Cl^- \ .$$
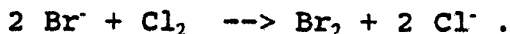
25   The bromine is then stripped from the acidified,
chlorinated seawater in a air stripper. The dilute
bromine fog is reacted with sulfur dioxide and forms an
acid fog:

$$Br_2 + SO_2 + H_2O \ \text{-->} \ 2 \ HBr + H_2SO_4 \ .$$
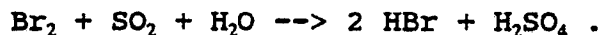
30   This acid fog is then condensed or absorbed and
introduced to a refluxed stripping column using, e.g.,
steam, to form a wet vaporous stream of HBr and a liquid
stream of H_2SO_4. The H_2SO_4 may be recycled to the initial
acidification step.   The vaporous HBr is mixed with
35   an oxygen-containing gas and heated to a temperature

between about 125°C and about 500°C. The heated gas
mixture is passed over the catalyst at conditions
suitable for the formation of bromine. The bromine is
then separated from the feed and co-produced water by
5   quenching, absorbing the Br_2 in a bromide salt solution
and desorbing pure Br_2. The Br_2 may be further dried, if
so desired.

Brief Description of the Drawings

10   Figure 1 shows a block diagram of a generic
embodiment of the inventive process.
             Figure 2 is a schematic diagram of a known
process for producing Br_2 from seawater.
             Figure 3 shows a schematic of a front end of a
15   process modified from the process shown in Figure 2
providing a feedstream for the processes shown in Figures
4 and 5.
             Figures 4 and 5 show preferred process
embodiments of this invention as terminal portions of the
20   Figure 3 process steps.
             Figure 6 is a graph of the performance of a
preferred HBr oxidation catalyst over a range of
operating temperatures.
             Figure 7 is a graph of the performance of a
25   preferred HBr oxidation catalyst over a period of time.

Description of the Invention

             As noted above, this invention is an improved
process for producing bromine from seawater. Several of
30   the steps of the process are from an older process in
wide use. The improvement largely involves an
intermediate catalytic step of oxidizing hydrogen bromide
with an oxygen-containing gas to form elemental bromine
according to the equation:
35           $4 \ HBr + O_2 \ ---> \ 2 \ Br_2 + 2 \ H_2O.$
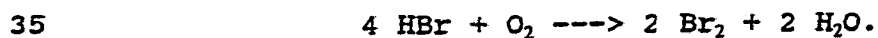
This step permits elimination of the chlorine oxidation step utilized in the older process.

Process

5   This invention is a process for producing Br_2 from seawater in which an intermediate catalytic step comprises oxidizing hydrogen bromide to that elemental bromine. The catalyst desirably comprises a supported copper or cerium bromide but may comprise a homogeneous
10   catalyst system generally as described below.

As is shown in Figure 1, in this process, seawater is screened of solid material such as seaweed and fish and is mixed with H_2SO_4 to produce an acidified stream having a pH between 3.0 and 3.5. This improves
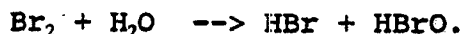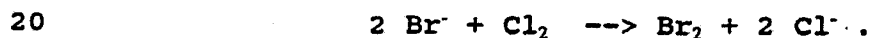15   bromine recovery by suppressing the hydrolysis of bromine as it is formed in a later step:

$$Br_2 + H_2O \longrightarrow HBr + HBrO.$$

The bromide ion in the seawater is then oxidized in the following step using chlorine:

20   $$2\ Br^- + Cl_2 \longrightarrow Br_2 + 2\ Cl^-\ .$$

The bromine is then stripped from the acidified, chlorinated seawater in an aerator or air stripper to form a dilute Br_2 fog and a bromine-depleted seawater stream. The dilute bromine fog is reacted with sulfur
25   dioxide and forms an acid fog:

$$Br_2 + SO_2 + 2\ H_2O \longrightarrow 2\ HBr + H_2SO_4\ .$$

This acid fog is then condensed or absorbed using a water or weak HBr stream. The absorbed acids are then introduced to a refluxed stripping column using, e.g.,
30   steam, to form a wet vaporous stream of HBr and a liquid stream of aqueous H_2SO_4. The H_2SO_4 may be recycled to the initial acidification step. The vaporous HBr is mixed with an oxygen-containing gas and heated to a temperature between 125°C and about 500°C. The heated gas mixture is
35   passed over the catalyst at conditions suitable for the

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formation of bromine. The reactor effluent is then
quenched and the bromine separated from the feed and co-
produced water. The Br_2 may be further dried, if so
desired.

5   Figure 2 shows a widely used variation of a
process for producing Br_2 from seawater. The bromine
content of seawater varies throughout the oceans of the
world but often is in the range of about 50 to 70 ppm.
The bromine typically is completely ionized or nominally
10   in the form of a salt such as NaBr.

The process involves introducing the seawater
through a pipeline (202) into a solids separator (204)
such as a screen or filter to remove large or entrained
solids, e.g., seaweed, fish, mud and sand. The filtered
15   seawater is then transported via line (206) and
thoroughly mixed with a H_2SO_4 stream (210) in that line
(206). The pH level of the liquid in line (206) is
maintained at about 3.0-3.5 so to prevent hydrolysis of
produced Br_2. The form of mixing line (206) is obviously
20   not critical but need only be substantially resistant to
corrosion at the noted conditions. The acidified
seawater is then mixed with a chlorine stream (212). The
bromide ion in the seawater is oxidized using that
chlorine in the following manner:
25               $2\ Br^- + Cl_2\ \longrightarrow\ Br_2 + 2\ Cl^-$.
The resulting stream (214) is then sent to a packed
stripping column (218) where a stream of air (216) is
utilized to strip the bromine from the liquid. The
resulting water stream (220) is then properly disposed
30   of, typically by returning it to the sea. The vapor
stream (222) from aerator (218) is a very dilute stream
of Br_2 and water usually in the form of a saturated vapor
or "fog" in air. This vapor stream (222) is then mixed
with sulfur dioxide (224) and forms a dilute acidic
35   vaporous stream (226) of hydrobromic and sulfuric acids:
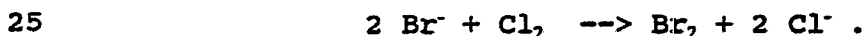
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$$Br_2 + SO_2 + 2 H_2O \longrightarrow 2 HBr + H_2SO_4 \; .$$
This acid stream (226) is contacted with a water stream
(232) in absorber (230). The air stream (234) is
relatively clean; it may be recycled if so desired. The

5   resulting aqueous H_2SO_4/HBr stream (236) is then of
sufficient strength to be efficiently oxidized.

The preceding steps are common both to the well
known process and to our improved process. Our
improvements are to the latter stages of the process

10   scheme and will be described in more detail below.
However, to allow a proper perspective, we will describe
the remainder of this widely recognized process as is
shown in Figure 2.

The aqueous H_2SO_4/HBr stream (236) is optionally

15   heated in exchanger (238) by feed/effluent exchange with
the heated effluent stream (246) and mixed with a second
chlorine stream (240) again to oxidize the bromine ion; a
portion of the chlorine is introduced through line (241)
to the bottom of stripping column (242):

20                $$2 \; Br^- + Cl_2 \longrightarrow Br_2 + 2 \; Cl^- \; .$$
The bromine is then stripped in a steam stripper (242).
The steam (244) in steam stripper (242) separates the
incoming stream into a liquid sulfuric acid/hydrochloric
acid stream (246) and a gaseous Br_2 stream (248)

25   containing some Cl_2 and H_2O vapor. The gaseous $Br_2/Cl_2/H_2O$
is condensed in exchanger (249). A water phase
(containing some Br_2) (262) from decanter (254) is used
as reflux in column (242).

The Br_2 product (260) is discharged from the

30   bottom of the decanter (254) through line (260) into the
purification unit (255). The purification unit (255) is
used to remove chlorine for recycle via line (261) and
drying of the Br_2 product. The Br_2 product is discharged
from the unit in line (263). After drying and chlorine

35   removal, the Br_2 product stream (263) is suitable for use

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in that it contains only about 0.5-1.0 % water, but is often subjected to a drying step by contact with a strong (93-97 %) sulfuric acid stream.

5   In contrast to the process described just above, our process eliminates the necessity of introducing additional chlorine at (240) and (241) to oxidize the bromide ion to Br_2 and instead utilizes an oxidation step using O_2 or air to produce the Br_2 product. In practical terms, nearly half of the chlorine

10   requirement of the prior art process is eliminated by use of our process.

        Figure 3 shows a front end portion of our inventive process adapting several stages of the prior art process mentioned above and suitable for producing an

15   HBr stream which may be used in our catalytic oxidation stage as described below with respect to Figures 4 and 5.

        In the process shown in Figure 3, the solids separator (204), mixing line (206), stripping column or aerator (218), and absorber (230) are all used as in the

20   process shown in Figure 2. In our inventive process, however, the aqueous H_2SO_4/HBr stream (236) is subjected to a steam stripping step in stripper (302). In addition to the steam (304), the stripper utilizes a small reflux to prevent sulfuric acid entrainment in the overhead

25   HBr/H_2O (308) stream. The bottom stream (310) is typically aqueous sulfuric acid and may be used to acidify the seawater in the front end of the process. The overhead HBr/H_2O (308) stream may be subjected to an SO_2 removal step (312) using an appropriate adsorbent or

30   a combination of a condenser to condense the HBr/H_2O stream, an oxidation step of converting the SO_2 to H_2SO_4 by reaction with introduced Br_2, and a reboiled stripper column to strip HBr from the resulting liquid stream. This step may be desirable only if there is a trace of

35   SO_2 remaining in the feedsteam. The resulting HBr stream

(314) may then be applied to the oxidation stages shown
below.

Figures 4 and 5 show desirable integrated
processes for the oxidation of HBr to Br_2 using the
catalyst described above. Figure 4 shows a process using
reasonably pure O_2 as the process feed; Figure 5 shows a
process in which air is the process feed.

The oxidation step involves the simple
expedient of mixing the gaseous or vaporous HBr from the
feed preparation step with a suitable amount of an
oxygen-containing gas, such as air, oxygen-enhanced air,
or oxygen and passing the mixture to the catalyst. The
O_2 is desirably added in an amount producing an $HBr:O_2$
molar ratio of between about 3.00 and 4.25. The O_2 may
be present in excess not only to assist in the HBr
oxidation but also to oxidize any hydrocarbonaceous
materials present in the feedstream. Nevertheless an
$HBr:O_2$ molar ratio of between above 3.9 and up to 4.1 is
preferred.

In any event, the $HBr-O_2$ mixture is then passed
through one or more beds of the catalysts described
above. As noted elsewhere, this reaction is highly
exothermic. The temperature in the reactor may be
controlled in a variety of ways. For instance, if an
adiabatic reactor is desired, the feed HBr likely will
need be diluted with steam, nitrogen, air, product stream
recycle, or the like to prevent excessive temperature
rise in the reactor. Specifically, the HBr feedstream
may have an HBr content of between 25% and 99.5% (wt) but
desirably has an HBr content between 35% and 55% (wt) but
most preferably between 45% and 55% (wt). Use of
anhydrous (or highly concentrated) HBr and pure O_2 as the
oxidant is difficult in that the temperature rise in an
adiabatic reactor is nearly 2000°C; even the use of air
and anhydrous HBr results in an adiabatic temperature

rise of 1000°C -- a possible but unlikely candidate for
ease of operation. Consequently, the use of air and an
HBr feed of between 45% and 55% (wt) is very desirable
and readily operable.

5   In other reactor configurations, some provision
may be made for removing or controlling the heat of
reaction, e.g., by inclusion of the bed or beds in an
appropriately cooled heat exchanger (such as by tubes of
catalyst in a steam generator), by adding the oxygen-
10   containing gas in a series of steps with cooling steps
amongst sequential catalyst beds, etc. The catalyst bed
or beds may be fluidized or ebullated if so desired.
Fluidization allows superior control of the bed
temperature and prevents the occurrence of "hot-spots"
15   in the catalyst.

          The materials of construction for the reactor
should be selected using normal materials criteria but
bearing in mind that the system is fairly corrosive. For
instance, if the reactor is operated at the lower end of
20   the reaction range noted above and the reactor is a
nickel alloy, the reactor should be maintained above the
temperature of condensation lest liquid phase corrosion
occur. Similarly, the upper range of temperature should
be controlled to prevent vapor phase corrosion. If a
25   ceramic system is chosen, similar criteria are applicable
to prevent dissolution of the ceramic or to prevent creep
of the polymeric seals used at joints and flanges.

Oxygen Process

30   In the embodiment of the inventive oxidation
process shown in Figure 4, an HBr stream (314) is
introduced from the front end process shown in Figure 3.
The HBr feedstream (preferably of about 48% HBr in water)
is sent to an evaporator (404) and to a superheater
35   (406). The resulting HBr vapor should be at a

temperature of about 230-250°C. The oxygen feedstream
(408) is similarly warmed to about 230-250°C with
superheater (410). The heat for superheaters (406) and
(410) may, for instance, be supplied by a circulating
5   hot oil system including hot oil heater (412).

The heated HBr feedstream and the heated oxygen
feedstream are then mixed to form a reactor feedstream
(414) which is then introduced into reactor (416). The
reactor (416) is desirably of a multi-tube design
10   containing the catalyst or may be of a multi-bed design.
Since the reaction is quite exothermic, reactor designs
which are capable of removing the heat of reaction from
the catalyst mass are obviously very desirable. The
reactor design shown is also used as a steam generator.

15   The reaction product stream (418) may then be
cooled in two stages. The first stage of cooling (420)
shown is a desuperheater and merely lowers the
temperature of the stream down to the neighborhood of the
stream's dew point, e.g., about 150°C. This stream is
20   then condensed and cooled to a temperature of about 40°C
in condenser (422).

The condensate is then separated into a liquid
Br_2 stream (424) saturated with water, a water stream
(426) saturated with Br_2, and a vaporous vent stream
25   (428) containing unreacted oxygen, bromine, water, and a
small amount of inerts. The device used for that
separation (430) may be a simple phase separation device
such as a decanter. Other density separation devices are
just as suitable.

30   The vapor stream (428) is then chilled in
refrigeration unit (432) to a temperature sufficient to
remove most of the Br_2 found in the vent stream. The
condensed Br_2 stream is separated in drum (432) and the
resulting Br_2 stream (434) is mixed with Br_2 stream (424)
35   for further processing. The resulting non-condensed

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oxygen vapor stream (436) is scrubbed in a gas treater
(438) using, for instance, sodium hydroxide remove any
remaining Br_2 before the treated oxygen is vented (440)
into the atmosphere. The vent gas treatment step may be
5   omitted and recycled into the reactor (416) if the oxygen
is of sufficient purity.

        The aqueous stream (426) coming from the
separator (432) is then stripped of its Br_2 content in a
distillation column (442). Distillation column (442)
10   produces two streams. The overhead vapor stream (444) is
condensed in overhead condenser (446) and collected in
reflux drum (448). The reflux drum (448) is a decanter
design. The lighter phase is largely water and is
recycled to the distillation tower (442) as reflux. The
15   heavier phase is Br_2 and the stream (450) is mixed with
other Br_2 streams, (424) and (434), for further treatment
such as by drying with strong H_2SO_4 in a countercurrent
absorption tower (456). The tower produces a weaker H_2SO_4
stream and the desired Br_2 product stream (458).

20   The bottom stream (452) from distillation tower
(442) is partially reboiled in reboiled in reboiler
(454). The remainder of the stream is mostly water
containing unconverted HBr feed and the water of reaction
formed in the reactor (416). All or a portion of this
25   stream may be treated by neutralization with, e.g.,
caustic soda, to produce a waste water stream (462). If
the inventive process is used as an integrated portion of
a process which is capable of using a dilute HBr, the
dilute HBr stream may be so recycled.

30   There are other ways of eliminating the water
produced in the reactor. For instance, by operating
separator (432) at different conditions, e.g., at a
temperature above 40°C, the overhead stream (436) will
contain the water of reaction.

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Air Process

The oxidation process step is preferably
operated using a less concentrated oxygen feedstream,
e.g., air or oxygen-enriched air. This variation is
5   shown in Figure 5.

In a general sense, the process scheme is
similar to that used in the oxygen process stage
described above. The reactor and condensation sections
are identical.

10   As above, an HBr feedstream (314) is sent to an
evaporator (504) and to a superheater (506). The air
feedstream (508) is compressed in compressor (509) and
heated in superheater (510). The heat for superheaters
(506) and (510) may, for instance, be supplied by a
15   circulating hot oil system including hot oil heater
(512). -

The heated HBr feedstream and the heated oxygen
feedstream are then mixed to form a reactor feedstream
(514) which is then introduced into reactor (516). The
20   reactor (516) is desirably of a design similar to that
described above although because of the additional
diluent in the feedstream is a little less sensitive to
reactor design, but those which are capable of removing
the heat of reaction from the catalyst mass are obviously
25   very desirable.

The reaction product stream (518) may then be
cooled in two stages. The first stage of cooling (520)
shown is a desuperheater and lowers the temperature of
the stream down to the neighborhood of the stream's dew
30   point, e.g., about 150°C. This stream is then condensed
and cooled to a temperature of about 40°C in condenser
(522).   The condensed reactor product stream (524) is
fed to a phase separator (526) where it is separated into
an aqueous stream (528) saturated in Br_2 and containing

35

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any unconverted HBr and an overhead vapor stream (530)
containing all of the Br_2.

The aqueous stream (528) may be treated in a
manner similar to that discussed above. The aqueous
5   stream (528) coming from the separator (526) is stripped
of its Br_2 content in a distillation column (530).
Distillation column (530) produces an overhead vapor
stream (532) which is condensed in overhead condenser
(534) and collected in reflux drum (536). Water from the
10   drum is recycled to the distillation tower (530) as
reflux. The Br_2 stream (538) is mixed with other Br_2
streams for further treatment such as drying.

The bottom stream (540) from distillation tower
(530) is reboiled. The stream is mostly water and
15   contains unconverted HBr feed and the water of reaction
formed in the reactor (516). All or a portion of this
stream (542) may be neutralized to produce a waste water
stream (546) or maybe recycled via line (548).

Returning to the phase separator (526), the
20   overhead vapor stream (N_2, Br_2, and H_2O) may be introduced
into the bottom of an absorption column (550) where cold
(-15°C) lean NaBr brine (552) is fed to the top to act as
absorption media for Br_2. The overhead stream (554) is
substantially free of Br_2.

25   The bottom stream (556) is heated (preferably
in feed-effluent heat exchanger (558) with the heat from
the bottom of stripper column (560)) and introduced into
stripper column (560). In that column, Br_2 is stripped
from the NaBr brine into an overhead stream (562). That
30   steam is condensed in exchanger (564) and collected in
reflux vessel (566). The water stream is decanted in
reflux vessel (566) and is both used as reflux in
stripper tower (560) and in the feed to distillation
tower (530).

35

     The vapor line (568) from the reflux drum (566)
may be mixed with the overhead vapor stream (554) from
absorber (550) and treated by neutralization in absorber
(570) to remove any remaining HBr before disposing of the
5 N₂ via vent (572).

     The decanted Br₂ (574) from reflux vessel (566)
may be mixed with the Br₂ stream (538) from reflux vessel
(536) and treated with concentrated H₂SO₄ in absorber
(576) to remove water and produce the dry product Br₂.
10

The Catalyst

     Catalysts suitable for this process include a
wide variety of supported or homogeneous materials. For
instance, the active catalyst may be selected from the
15 metals; and the oxides, halides (particularly chlorides
and bromides), and oxyhalides of the following metals:
Group IB (particularly Cu), Group IVB (particularly Ti
and Zr), Group VB (particularly V), Group VIB
(particularly Cr,Mo, and W), Group VIIB (particularly Mn
20 and Re), Group VIII (particularly Fe, Co, Ni, Pt, And
Pd), and the rare earth lanthanide series (particularly
Ce). The active catalyst may be promoted with one or
more Group IIA metals (particularly Ca) or lanthanides,
if so desired. The active catalyst and the promoter,if
25 any, may be supported on known catalyst supports such as
MgO, Al₂O₃ (particularly in eta- or delta-form), ZrO₂,
HfO₂, SiO₂ (particularly in silica gel form), clays such
as bentonite or attapulgite, and natural materials such
as pumice.
30   The active catalysts listed above should be
present in at least a catalytic amount, that is to say,
an amount sufficient at least to catalyze the reaction of
HBr and oxygen to produce Br₂. Active catalytic metals,
depending upon the metal selected, may be present in the
35 amount of 0.1 % to 35 % (by weight) of the overall

composition is desirable; 1.0 % to 20 % (by weight) of
catalytic metal is more desirable and 3.0 % to 10.0 %
(by weight) of catalytic metal is most desirable.

5   The promoters/stabilizers may be any salt or
complex of the noted metals, whether oil or water
soluble, which can be impregnated onto the catalyst
support or mixed with the support, e.g., as by ball
milling with the support precursor. The bromide salts
are especially suitable, but other halides (iodide or
10   chloride), oxyhalides, oxides, phosphates, sulfides,
sulfates; complexes such as acetylacetonates, and the
like are also suitable. The bromides, oxybromides,
oxides, and mixtures are useful and conveniently
available. The promoter/stabilizer metal-bearing
15   material should be present in an amount such that the
overall content (in whatever form) is desirably between
0.1 % and 10 % (by weight) of the overall composition;
1.0 % to 6.0 % (by weight) is more desirable; 1.0 % to
4.0 % (by weight) is most desirable.

20   If the catalyst support is zirconium-
containing, it desirably contains more than about 50%
(wt) of zirconia. A minor amount of other metal oxides,
e.g., alumina, titania, yttria, silica, hafnia, etc., may
be included as a binder or extrusion aid or to increase
25   surface area if so desired. Whether the support is
zirconium-containing or not, it is desirable to use a
support which has significant porosity in the range
between 30 and 100Å, e.g., > 0.01 cc/gm pore volume in
the range of 30 and 100Å.

30

Preferred Catalyst
        The preferred catalyst comprises promoted
copper bromide on a zirconia support. At the
temperatures of operation contemplated in this process,
35   the copper bromide does not substantially migrate from

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the catalyst composition nor among different regions of the catalyst and is very active. This high activity permits the use of comparatively lower temperatures thereby enhancing, even more, the catalyst's stability.

5   This preferred catalyst is produced by placing copper bromide directly onto the support, and is not made by converting another copper-bearing material into copper bromide on the support. Although we believe that the direct addition of the copper bromide to the support is

10   critical to the stability and activity of the catalyst, we do not wish to be bound to that theory. Additionally, the addition of certain promoters to the supported copper bromide catalyst appears to add substantial stability to the catalyst. Finally, although the support most

15   desirably comprises a zirconium-containing material such as zirconia, other supports are suitable.

           Specifically the preferred catalyst is a composite comprising or desirably consisting essentially of copper bromide; promoter/stabilizer selected from

20   materials containing one or more salts, oxides, or complexes of metals selected from Ca, Y, Nd, or La or of metals having an ionic radius between about 0.9 and 1.4 Å; and an oxidic zirconium-containing catalyst support. The preferred promoters are Nd and La. Most preferred is

25   La.

           The copper bromide should be present in at least a catalytic amount, that is to say, an amount sufficient at least to catalyze the reaction of HBr and oxygen to produce Br_2. We have found that copper bromide

30   in the amount of 0.1 % to 20 % (by weight) of the overall composition is desirable; 1.0 % to 6 % (by weight) of copper bromide is more desirable and 3.0 % to 6.0 % (by weight) of copper bromide is most desirable.

           We have found that the introduction of the

35   copper catalyst onto the zirconium-containing catalyst

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support in the form of copper bromide results in a
catalyst composition which is both more stable and more
active than compositions in which the catalyst is
introduced in another form, such as by the oxide. We

5   have additionally found that the x-ray diffraction
spectrum (Cu_{α}) of the catalyst composition does not show
the presence of crystalline $CuBr_2$. Specifically, the x-
ray diffraction spectrum of crystalline $CuBr_2$ contains
the following lines:

10

2θ (°)	I/I_0
14.485	1.0
29.063	1.0
36.041	0.85

15
The absence of the most distinctive line ($2\theta = 14.485°$)
demonstrates the substantial absence of copper bromide
crystallinity. Catalyst compositions prepared using CuO,
which converts to copper bromide in the HBr oxidation

20   process, show the presence of that distinctive line ($2\theta =$
14.485°) . We believe this to indicate that the copper
bromide introduced to the zirconium-containing support,
in contrast to copper bromide produced on the support
from another material, is essentially amorphous.

25   We have not, however, found the source of the
promoters/stabilizers to be of significant importance.
Any salt or complex of the noted metals, whether oil or
water soluble, which can be impregnated onto the
zirconium-containing support or mixed with the zirconium

30   support, e.g., as by ball milling with the zirconium
support precursor, is suitable. The bromide salts are
especially suitable, but other halides (iodide or
chloride), oxyhalides, oxides, phosphates, sulfides,
sulfates; complexes such as acetylacetonates, and the

35   like are also suitable. Lanthanum bromide, oxybromide,

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oxide, and mixtures are useful and conveniently
available. The promoter/stabilizer metal-bearing
material should be present in an amount such that the
overall content (in whatever form) is desirably between
5   0.1 % and 10 % (by weight) of the overall composition;
1.0 % to 6.0 % (by weight) is more desirable; 1.0 % to
4.0 % (by weight) is most desirable.

The zirconium-containing support typically
should contain more than about 50% (wt) of zirconia. A
10   minor amount of other metal oxides, e.g., alumina,
titania, yttria, hafnia, silica, etc., may be included as
a binder or extrusion aid or to increase the surface area
or porosity if so desired. We have found that it is very
desirable to use a zirconia support which has significant
15   porosity in the range between 30 and 100Å, e.g., > 0.01
cc/gm pore volume in the range of 30 and 100Å.

General

The catalyst material may be utilized in any
20   physical form convenient to the process in which it is
utilized. Such forms may include tablets, extrudates,
raschig rings, Pall rings, or the like. The reaction is
very exothermic and consequently the relative external
surface area may be an important consideration in some
25   reactor/process configurations.

The catalyst desirably is prepared by
dissolving the appropriate catalyst metal and the
promoter/stabilizer metal compounds or complexes
independently in aqueous acid, preferably HBr, solutions
30   and impregnating them into the catalyst supports. The
catalyst supports should be dried at, e.g., 110° to 135°C
in air, before impregnation so to allow accurate
measurement of the metal content added to the support.
The method and sequence of impregnating the support has
35   not been found to be critical. If the various compounds

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are compatible, e.g., they don't react together and don't
precipitate from solution, a single solution containing
the metals may be used as the impregnating solution.
Depending upon the impregnating procedure chosen, the
5   solutions may be saturated or not. If an incipient
wetness method is selected, the amount of solution will
match the pore volume of the support requiring that the
composition of the solution be adjusted to assure that
the amount of metal added to the support is appropriate.
10   If other procedures are elected, saturated solutions may
be used and a particular amount of the solutions chosen.
         The impregnated support is dried and ready for
use.

15   The invention has been disclosed by direct
description. Below may be found a number of examples
showing various aspects of the invention. The examples
are only examples of the invention and are not to be used
to limit the scope of the invention in any way.
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EXAMPLES

Example 1

This example shows a long term test of the a
5   highly desired $CuBr_2/LaBr_3/ZrO_2$ catalyst in the HBr
oxidation step.

A pure zirconia support having a pore size
distribution of 0.093 cc/gm of pore volume in the range
of 30-100Å and 0.098 cc/gm in the range of 600-1000 Å
10   pore diameter was used to prepare the $CuBr_2/LaBr_3/ZrO_2$
catalyst. The support was a powdered zirconia support
which was impregnated with solutions of $CuBr_2$ and $LaBr_3$
and pressed in a die using a carved press. This pressing
was then ground and sieved to give a 20-30 mesh fraction.
15   The finished catalyst contained 0.2 mmoles/cc of $CuBr_2$
and 0.6 mmoles/cc of $LaBr_3$. The pore size distributions
were determined using a Micromeritics Autopore II 9220
mercury porosimeter.

The catalyst was tested for activity using the
20   following procedure:

A 1 cm OD by 45 cm long glass reactor tube was
filled to about its length-wise center with glass beads.
A glass wool plug was then inserted. About 1 cc of
catalyst was placed on the glass wool. Another glass
25   wool plug was placed over the catalyst bed. The
remainder of the glass tube was packed with glass beads.
The glass reactor was then placed in a tube furnace with
an aluminum sleeve between the outer reactor wall and the
inner wall of the furnace to aid in heat distribution. A
30   thermocouple was included at the center of the catalyst
bed. A 48% HBr solution was delivered to the reactor at
a rate of 6 cc/hr using a syringe pump. During the test,
the syringe pump had to be refilled about every 20 hours.
During the refilling period, nitrogen flowed through the
35   reactor. Upon readmittance of HBr to the reactor, an

initially lower reaction rate was observed in the first
20 minutes of testing. However, the rate then returned
to the rate prior to the refilling of the syringe.
Oxygen was fed to the reactor using a mass flow
5 controller at a rate of 6 cc/hr. The temperature of the
reactor was maintained at 275°C.

   The reaction products and unreacted feed
materials were condensed in traps containing KI. In the
traps, the product Br_2 formed reacts there with the KI to
10 form the I_3^- ion. The I_3^- ion was then titrated with
$Na_2S_2O_3$. The amount of bromine formed in the reactor was
calculated from the titration results. The reactor
effluent was collected in the traps, measured at various
intervals, and the reaction rates calculated. The
15 measured rate at intervals over the 100 hours is shown in
the Table. The data show no decrease in activity over
the 100 hour run, and perhaps show some increase in
activity during that period. This indicates good long
term life for the $CuBr_2/LaBr_3/ZrO_2$ catalyst.

20

Table	
Time on Stream (hrs)	Rate ($\mu mol\text{-}cc^{-1}\text{-}sec^{-1}$)
2	2.7
20	3.2
50	2.9
80	3.7
100	4.1

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Example 2

This example shows the use of the preferred $CuBr_2/LaBr_3/ZrO_2$ oxidation catalyst in the temperature range between 150°C and 350°C.

The catalyst was tested as in Example 1; again, the rate of 48% HBr feed was 6 cc/hr, and the rate of O_2 feed was 6 cc/min. The temperature was varied to produce bed temperatures ranging from 150° to about 350°C. Figure 6 shows the average reaction rates for the catalyst as a function of temperature for a 2 hour test.

Example 3

This example shows the use of an homogeneous catalyst system for conversion of HBr to Br_2. A 250 ml Fisher-Porter bottle equipped with an overhead stirrer was charged with 30 g Cu_2Br_2 (as catalyst) and 110 ml of 48% HBr. The assembly was placed in an oil bath and brought to about 135°C. The stirring rate was 750 rpm. Anhydrous HBr was metered to the reactor at 350 ml per minute and O_2 was fed at 750 ml per minute. The total pressure was maintained at 50 psig. A gas stream continuously stripped any Br_2 formed in the system, which Br_2 was trapped downstream using a KI trap. The trap operated to detect the amount of Br_2 formed in the reactor by reacting with the Br_2 to form the I_3^- ion. The I_3^- ion was titrated with NaS_2O_3 and the amount of produced Br_2 was calculated using the result. The traps were checked about every ten minutes. Figure 7 shows the rate of Br_2 production as a function of time. This example shows the effectiveness of the catalyst in oxidizing HBr to Br_2.

This invention has been described using examples to show preferred embodiments. It will be apparent to those skilled in the art that modifications

and changes may be made which still fall within the spirit and scope of the attached claims.

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WE CLAIM AS OUR INVENTION:

1. A process for producing Br_2 from seawater comprising the steps of:

    a.   acidifying the seawater with sulfuric acid,

    b.   chlorinating the acidified seawater,

    c.   aerating the acidified, chlorinated seawater to produce a bromine depleted seawater stream and a dilute H_2O/Br_2 stream,

    d.   mixing the dilute H_2O/Br_2 stream with SO_2 to form an acid stream comprising HBr, H_2SO_4, and air,

    e.   separating the air from the remainder of the acid stream,

    f.   separating the HBr from the H_2SO_4 and forming a HBr reactor feedstream,

    g.   contacting the HBr reactor feedstream and an O_2-containing gas with a catalyst composition to convert at least a portion of the HBr to Br_2 and produce a reaction effluent stream, and

    h.   recovering the Br_2 product.

2. The process of claim 1 where the catalyst composition comprises an active catalyst selected from the metals, and oxides, halides, and oxyhalides of the following metals: Group IB, Group IVB, Group VB, Group VIB, Group VIIB, Group VIII, and the rare earth lanthanide series.

3. The process of claim 2 where the catalyst composition additionally comprises a promoter and a catalyst support selected from MgO, Al_2O_3, ZrO_2, HfO_2, SiO_2, bentonite, attapulgite, and pumice.

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4.   The process of claim 2 where the catalyst composition
is an homogeneous liquid.

5.   The process of claim 3 where the catalyst composition
comprises copper bromide, a promoter, and an oxidic
zirconium-containing catalyst support.

6.   The process of claim 5 where the copper bromide
content of the catalyst composition is within the range
of about 0.1 % to 20 % by weight.

7.   The process of claim 6 where the overall copper
bromide content of the catalyst composition is within the
range of about 1 % to 10 % by weight.

8.   The process of claim 7 where the overall copper
bromide content of the catalyst composition is within the
range of about 0.1 % to 6 % by weight.

9.   The process of claim 5 in which the promoter is
selected from compounds or complexes of Ca, Y, Nd, or La.

10.   The process of claim 9 in which the promoter is a
lanthanum-containing compound comprising lanthanum
bromide, lanthanum oxybromides, or a mixtures thereof.

11.   The process of claim 10 in which the promoter is
present in an amount between 0.1 % and 10 % (by weight)
of the catalyst composition.

12.   The process of claim 5 in which the zirconium-
containing catalyst support comprises zirconia.

13.   The process of claim 10 in which the zirconium-
containing catalyst support comprises zirconia.

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14. The process of claim 12 where the catalyst's x-ray diffraction graph shows substantially no peak at $2\theta = 14.485°$.

5   15. The process of claim 11 in which the porosity of the zirconia is greater than about 0.01 cc/gm pore volume in the range of about 30-100 Å pore diameter.

16. The process of claim 5 in which the molar ratio of
10    $HBr:O_2$ is between about 3.25 and 4.1.

17. The process of claim 16 in which the molar ratio of $HBr:O_2$ is between about 3.9 and 4.0.

15   18. The process of claim 1 in which the Br_2 product recovery is effected by quenching the reaction effluent in a quench stream containing HBr and removing unreacted HBr, absorbing Br_2 from the quenched reaction effluent in a stream containing aqueous NaBr to form a Br_2 absorbate
20   stream and a water phase, desorbing Br_2 from the Br_2 absorbate stream, decanting Br_2 from the water phase to produce a Br_2 product stream.

19. The process of claim 18 additionally comprising the
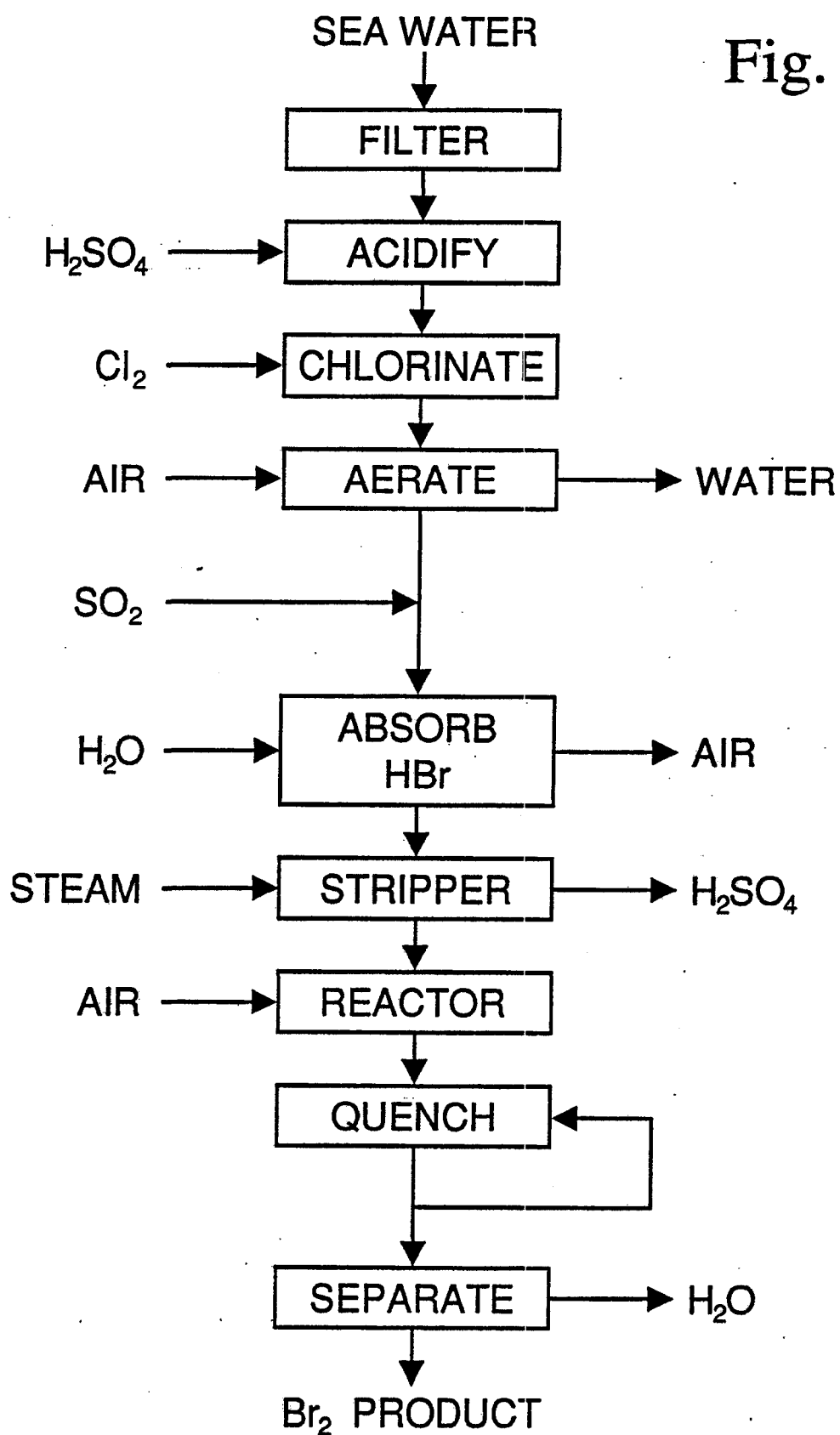25   step of drying the Br_2 product stream by contacting it with strong H_2SO_4.

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20.   A process for producing Br$_2$ from seawater comprising
the steps of:

a.   acidifying the seawater with sulfuric
     acid,

5   b.   chlorinating the acidified seawater,

c.   aerating the acidified, chlorinated
     seawater to produce a bromine depleted
     seawater stream and a dilute H$_2$O/Br$_2$
     stream,

10   d.   mixing the dilute H$_2$O/Br$_2$ stream with SO$_2$
     to form an acid stream comprising HBr,
     H$_2$SO$_4$, and air,

e.   separating the air from the remainder of
     the acid stream,

15   f.   separating the HBr from the H$_2$SO$_4$ and
     forming a HBr reactor feedstream,

g.   contacting the HBr reactor
     feedstream with an O$_2$-containing
     gas in a molar ratio of HBr:O$_2$

20   between about 3.25 and 4.1 with
     a catalyst composition
     comprising copper bromide in an
     amount such that the overall
     copper bromide content of the

25   composition is within the range
     of about 1 % to 10 % by weight,
     a lanthanum-containing compound
     selected from the group of
     lanthanum oxide, lanthanum

30   bromide, lanthanum oxybromides,
     or mixtures thereof, and a
     zirconia catalyst support to
     convert at least a portion of
     the HBr to Br$_2$ and produce a

35   reaction effluent stream, and

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      h.   quenching the reaction effluent in a
              quench stream containing HBr and removing
              unreacted HBr,

      i.   absorbing Br_2 from the quenched reaction
              effluent in an aqueous stream containing
              NaBr to form a Br_2 absorbate stream,

      j.   desorbing Br_2 from the Br_2 absorbate
              stream, and

      k.   decanting Br_2 from a water phase of
              produce a Br_2 product stream.

21.   The process of claim 20 additionally comprising the
step of drying the Br_2 product stream by contacting it
with strong H_2SO_4.

Fig. 1

SEA WATER

↓

FILTER

↓

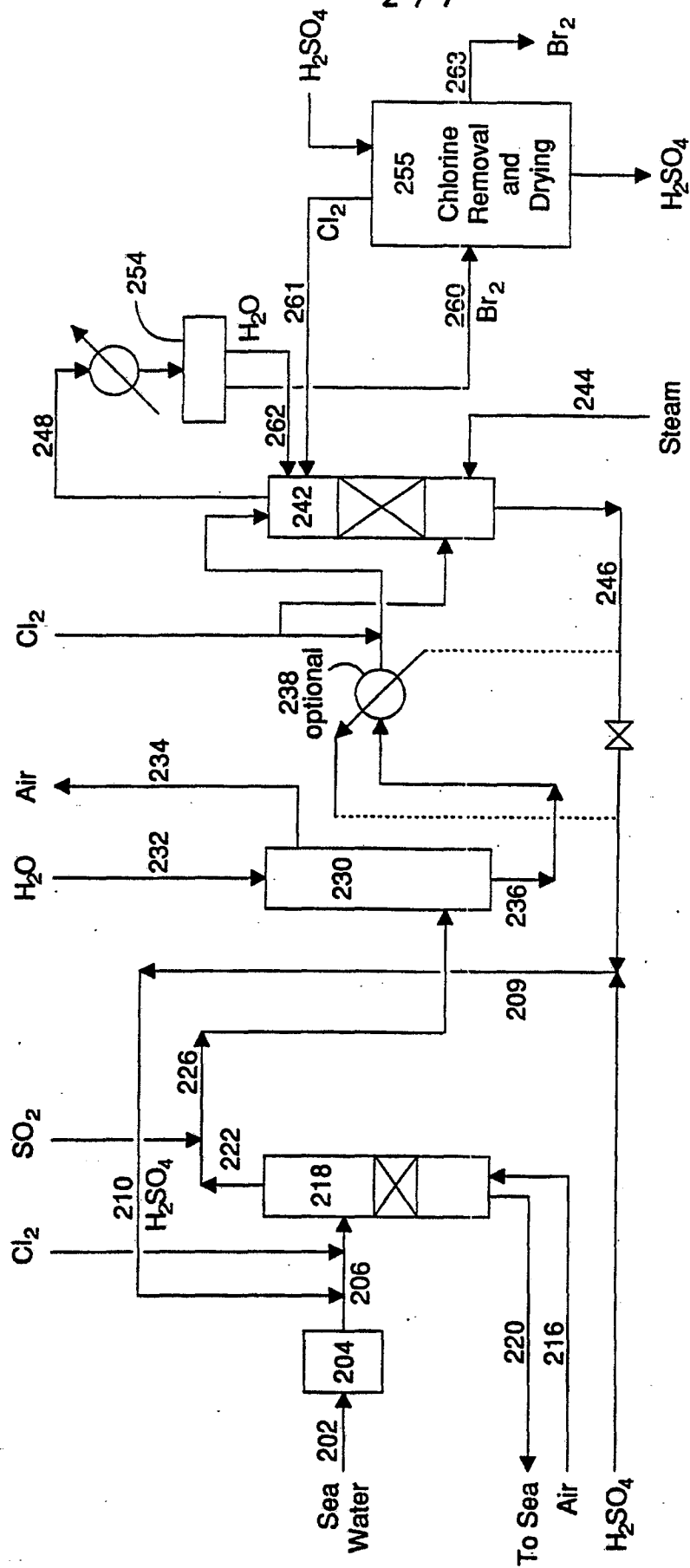H$_2$SO$_4$ ⟶ ACIDIFY

↓

Cl$_2$ ⟶ CHLORINATE

↓

AIR ⟶ AERATE ⟶ WATER

↓

SO$_2$ ⟶

↓

H$_2$O ⟶ ABSORB HBr ⟶ AIR

↓

STEAM ⟶ STRIPPER ⟶ H$_2$SO$_4$

↓

AIR ⟶ REACTOR

↓

QUENCH ←

↓

SEPARATE ⟶ H$_2$O

↓

Br$_2$ PRODUCT

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

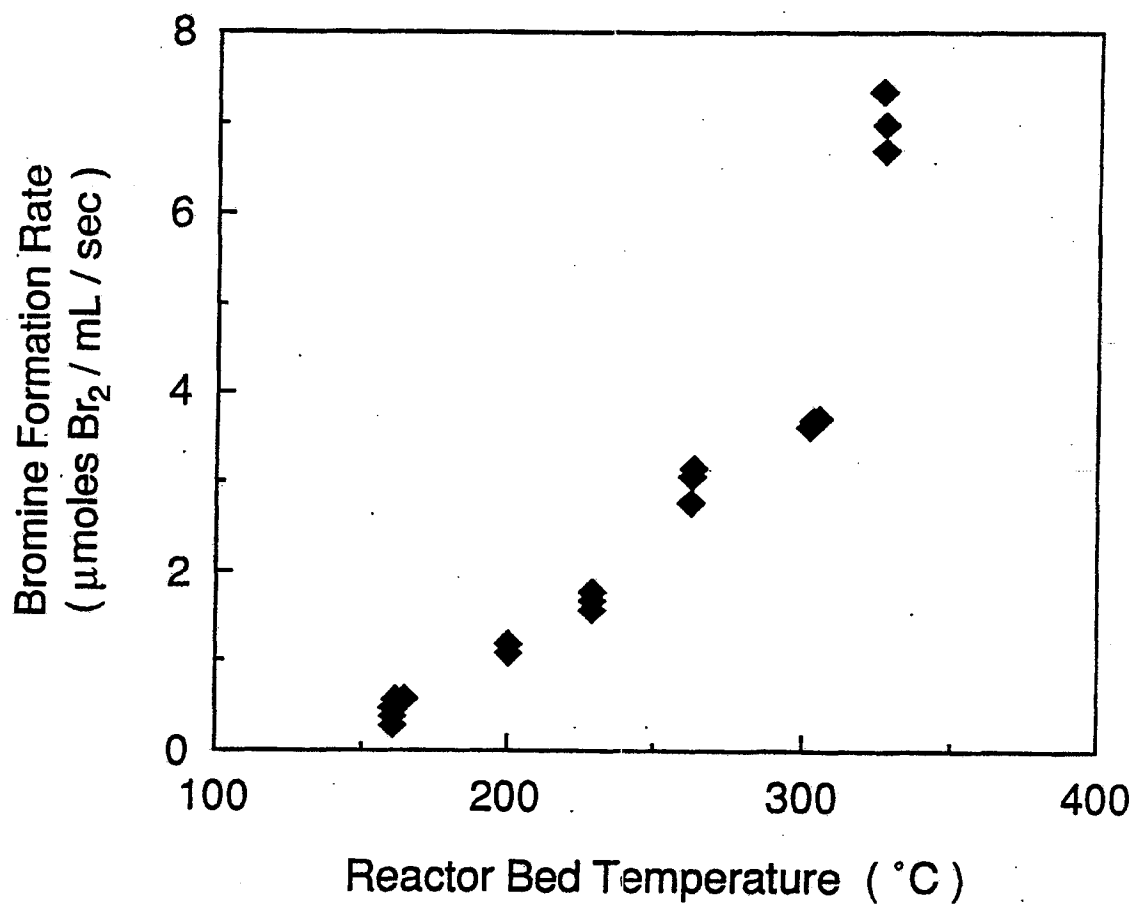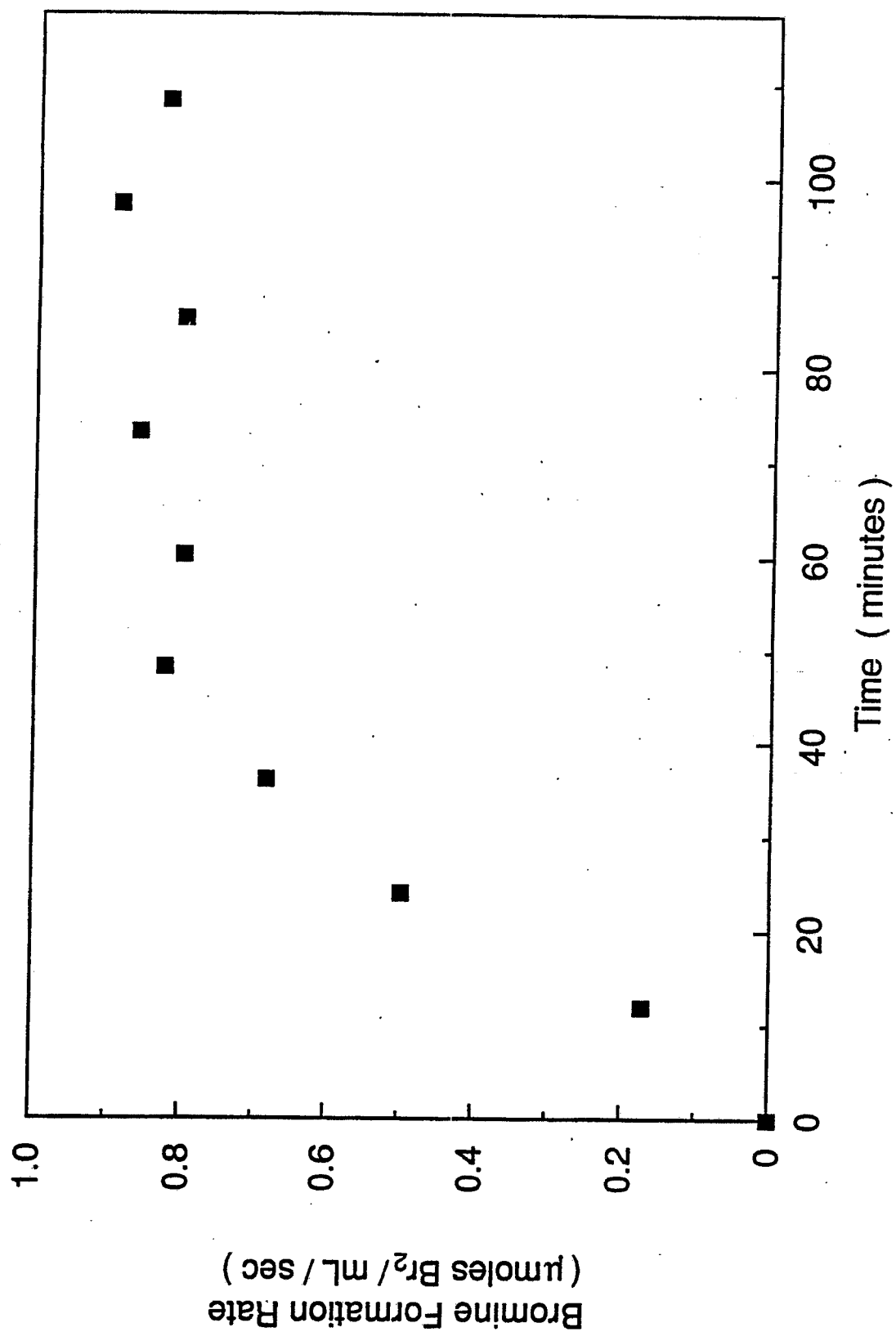Fig. 7

Time (minutes)

Bromine Formation Rate
(μmoles Br₂/ mL / sec)
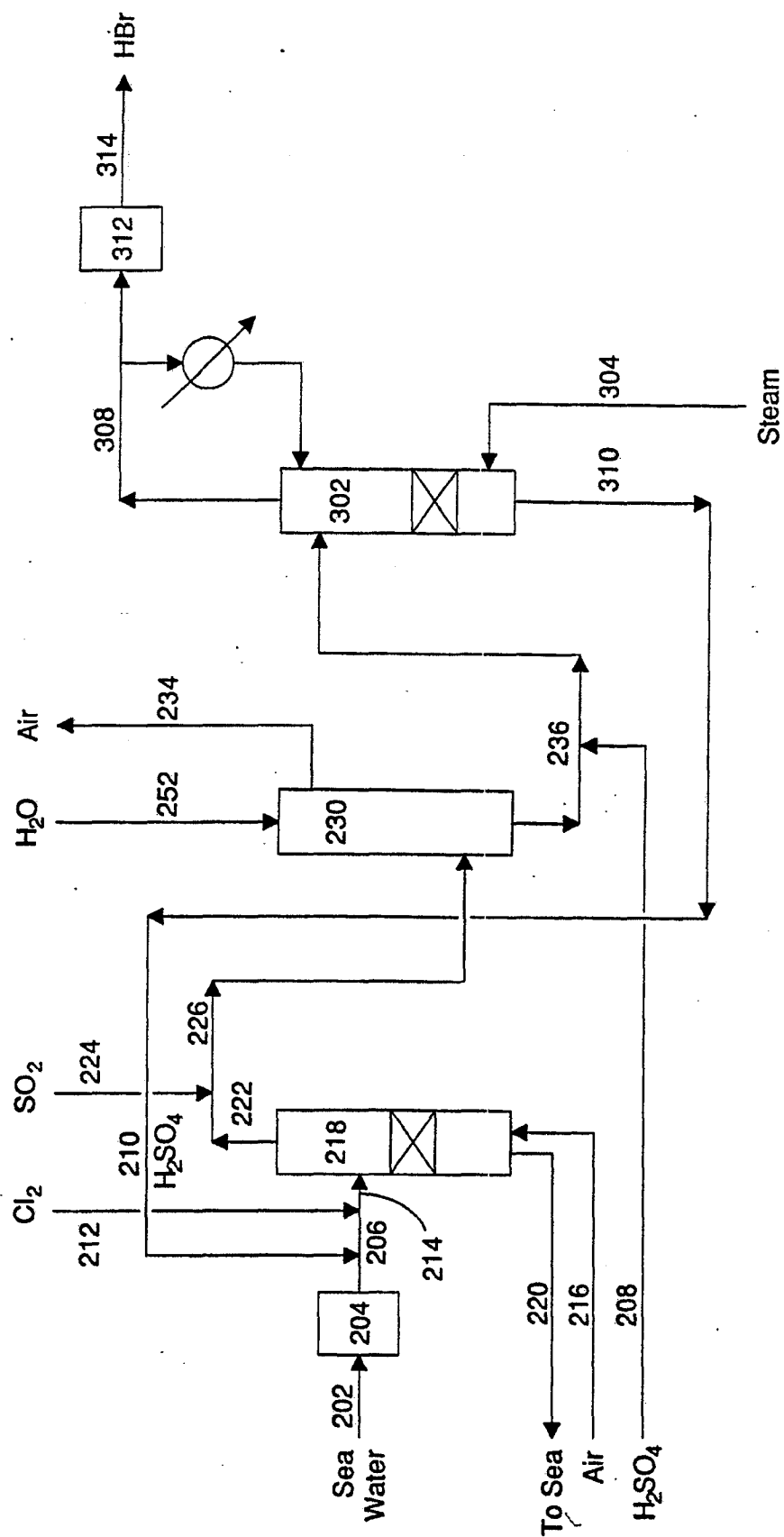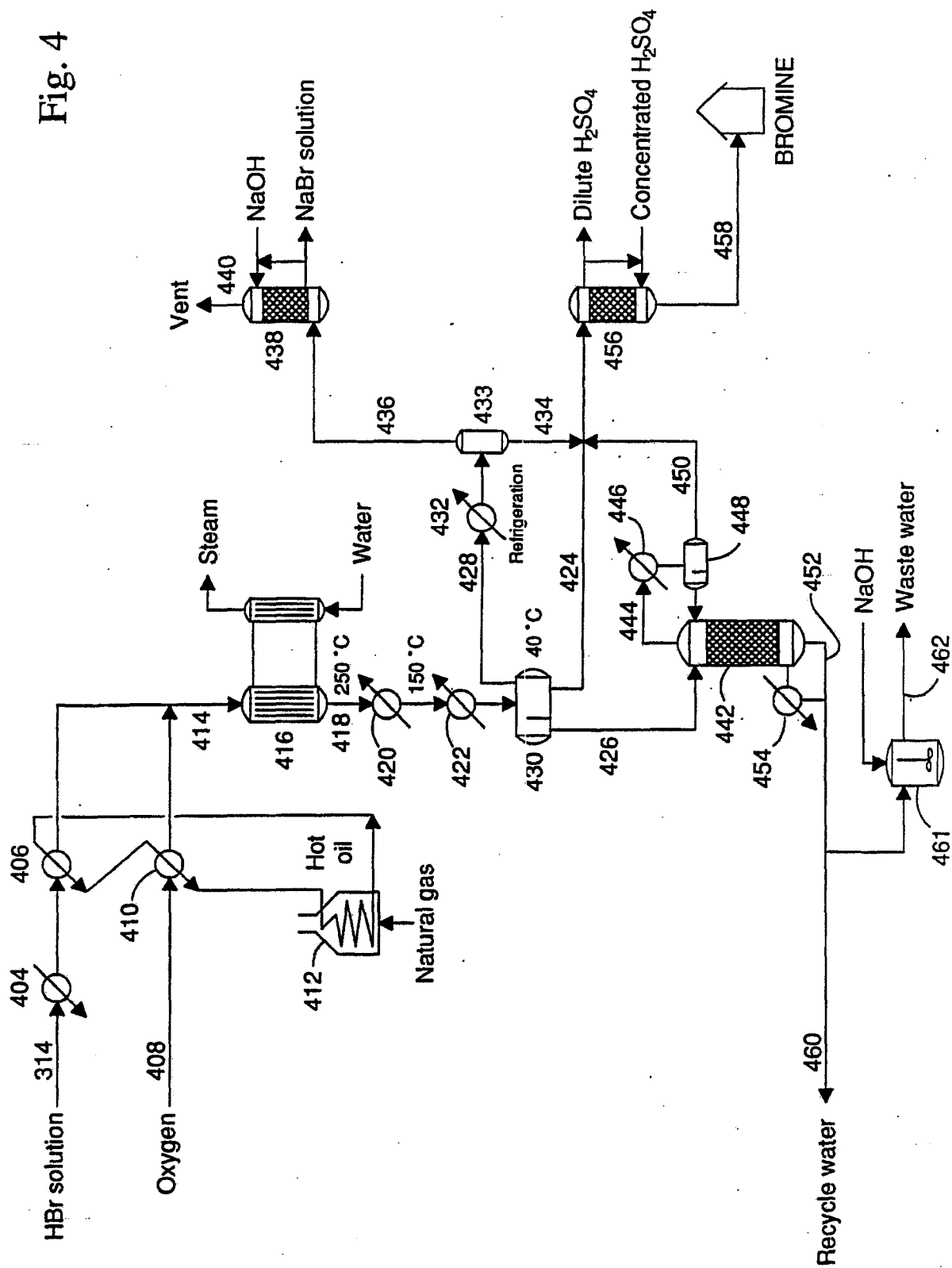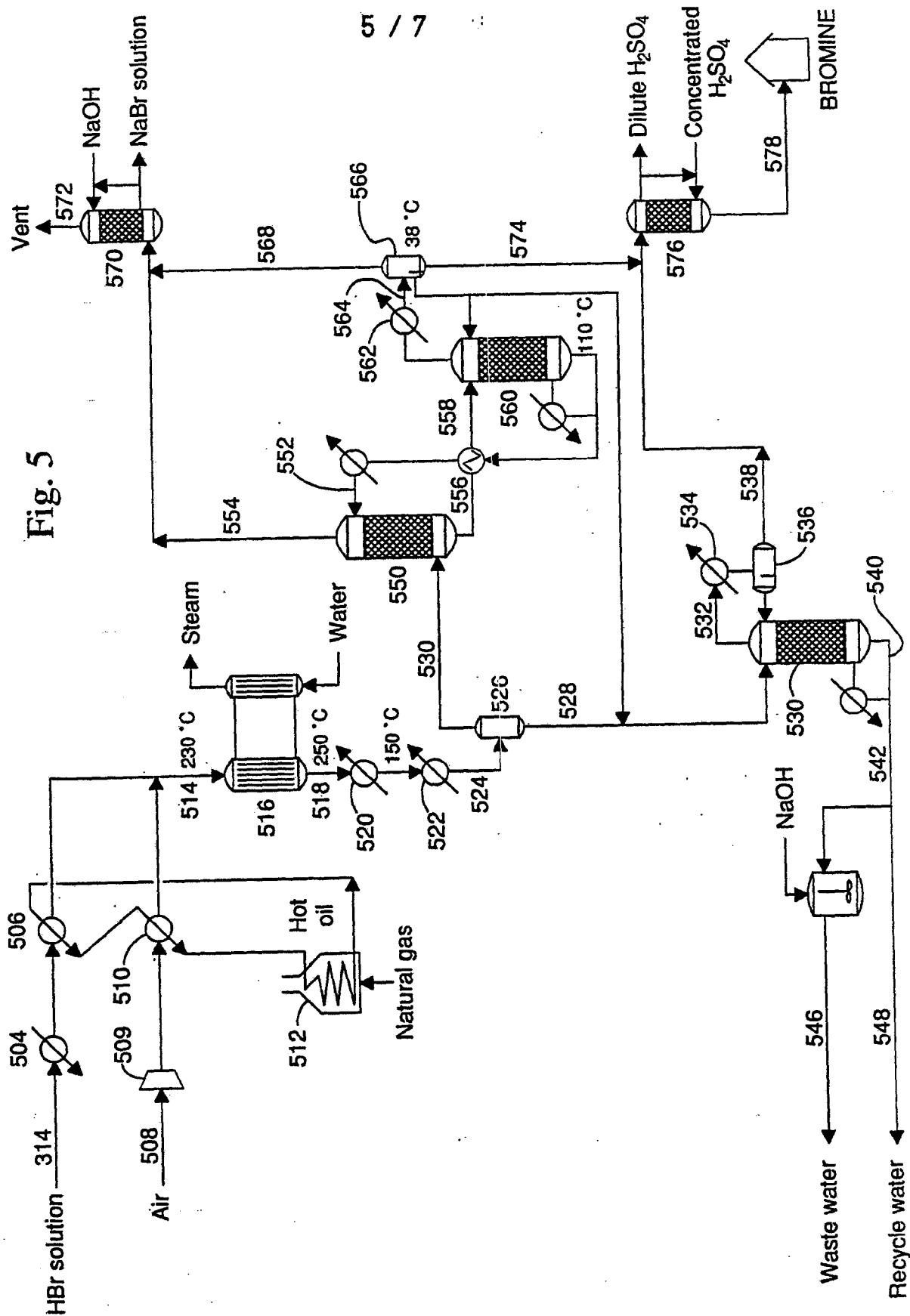
INTERNATIONAL SEARCH REPORT

PCT/US92/07822

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01B 7/09
US CL :423/502

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/500,423/503,423/488,423/481

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 2,536,457 (Mugdan) 02 January 1951, See column 1, line 24; column 2, lines 10-25, 40-46; column 3, lines 25-26, column 4, lines 30-70, column 5, lines 1-10 and figure.	1-4,18,20
Y	US,A, 2,143,233 (Heath) 10 January 1939 1936, See figure and claim 2.	1-4,18,20
Y	JP,A, 38-20358 (Shell) 03 October 1963, See column 1 and column 2.	5-17,20
Y	CA,A, 615,926 (Deahl, et al.) 07 March 1961, See column 1, lines 20-25 and column 2, lines 28-32.	5-17,20

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 NOVEMBER 1992	1 4 JAN 1993
Name and mailing address of the ISA/ Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer VALERIE ANN LUND
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-1304

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BE,A,651,747 (Ratkuv) 12 February 1965, See abstract.	19 & 21
Y	US,A, 2,163,877 (Hooker) 27 June 1939 See column 3, lines 1-25 and column 2.	1,20
A	US,A, 3,816,599 (Kafes) 11 June 1974, See column 3, lines 1-40.	1-20
A	US,A, 4,119,705 (Riegel) 10 October 1978 See abstract and claim 1.	1,20
A	FR,A, 1,291,932 (California Research) 19 March 1962, See abstract and column 2.	1,20
A	Chemical Engineering Science, Vol. 23, 20 February 1968 Ruthven, et al., "The Kinetics of the Oxidation of Hydrogen Chloride Over Molten Salt Catalyst" pages 981-988.	1,20